Technical Bulletin 120 April 1937

The Relative Toxicity of Insect Fumigants

H. H. Shepard, D. L. Lindgren, and E. L. Thomas
Division of Entomology and Economic Zoology

University of Minnesota
Agricultural Experiment Station

Accepted for publication, September 1936.

The Relative Toxicity of Insect Fumigants

H. H. Shepard, D. L. Lindgren, and E. L. Thomas
Division of Entomology and Economic Zoology

University of Minnesota
Agricultural Experiment Station

Accepted for publication, September 1936.

CONTENTS

THE RELATIVE TOXICITY OF INSECT FUMIGANTS[1]

H. H. Shepard, D. L. Lindgren, and E. L. Thomas

INTRODUCTION

Fumigation of stored products with either hydrocyanic acid gas or carbon disulfide has been a well-known practice for the last half-century. One of the earliest known insecticidal practices was the use of sulfur fumes. Altho carbon tetrachloride was suggested in 1910 (Morse) as a safe substitute for carbon disulfide, little advance was made in the field of fumigants until following the World War. Since then there has been a rather systematic search for compounds effective as insect fumigants.

The search has involved extensive studies of the relative values of many chemicals against a variety of insects. Moore (1917) tested a considerable list of chemicals against the house fly *(Musca domestica* L.). In this work he was the first to show the toxicity of chloropicrin (a tear gas used in the war) as an insect fumigant. Following the war some interest developed in the problem of using war gases as fumigants. All but chloropicrin were impractical for that use, it was decided.

Soon after the war the insurance companies and railroads ruled against the use of carbon disulfide because of the risk of explosion and fire. Because of this situation, the United States Department of Agriculture conducted tests on a large number of chemicals. Their toxicity was determined for grain and flour insects, because these pests constitute the greatest problem in the field of stored-product insect control. The first results were published in 1925 (Neifert *et al.*). Further work developed some new fumigants during the years up to 1929, particularly ethylene oxide and ethylene dichloride. Altho none of the newer fumigants are used in very large quantities as compared with the cyanide preparations, their aggregate sales are considerable.

The more noteworthy investigations of fumigants in recent years have been concerned with refinements in toxicity determination; with the influence of carbon dioxide, vacuum absorption, and other factors upon effectiveness; and with the relative toxicity of new chemicals, particularly those related to compounds already known to possess a fair degree of toxicity.

The subject of fumigant toxicity is an intricate one. The specificity of fumigant action was pointed out by Strand (1930): "One fumigant may outrank another when used against one particular species and fall below it when tested against other kinds of insects." This fact was enlarged upon by Shepard and Lindgren (1934). Temperature affects the toxicity of all fumigants, but some more than others. Moisture of the air and the stage of development and physiological condition of the insect are other factors of importance in this connection.

[1] Completion of this project was made possible by workers supplied on WPA Project 1985, Minnesota Works Progress Administration; sponsor, University of Minnesota.

DETERMINATION OF FUMIGANT TOXICITY

The determination of fumigant toxicity usually involves merely the introduction of the test insects into static mixtures of the fumigant and air. The liquid chemical is pipetted into the test flask which already contains the insects to be treated. If the chemical has a boiling point near or below room temperature it sometimes may be conveniently measured in a cold room. In this case its specific gravity at the lower temperature must be known.

In order to work with gaseous chemicals or their mixtures, some modification of the equipment is necessary. It has been customary to make the desired mixture of air and fumigant, then to draw it through a chamber containing the insects. For this dynamic technique, a series of flowmeters is necessary. R. M. Jones (1933) obviated this more complicated equipment by drawing the vaporized fumigants into evacuated fumigation flasks. The required quantities were measured in terms of pressure differences registered on a manometer.

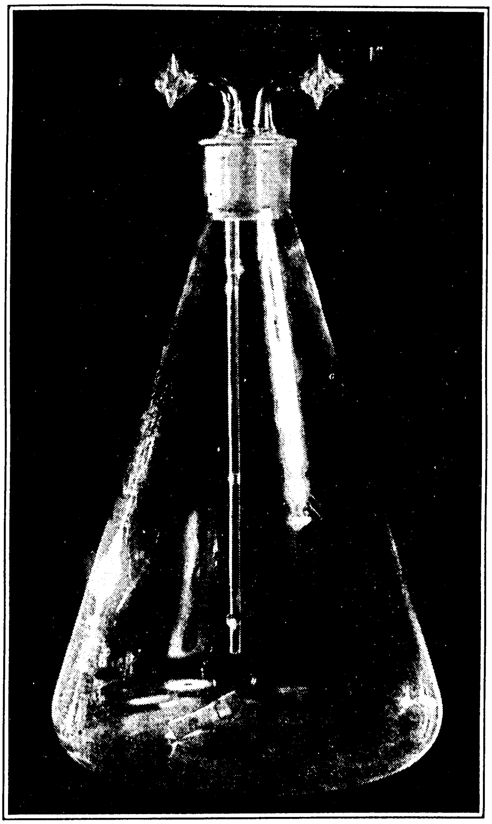

Fig. 1. Strand Fumigation Flask

The method used for determining the fumigant toxicities reported in this bulletin was described by Strand (1930) and by Lindgren and Shepard (1932). For fumigants with low boiling points the Strand fumigation flask was used (Fig. 1). This flask has two stopcock connections passing through a ground glass head. Small quantities of liquids, or gases from a gas burette, may easily be drawn into the partially evacuated flask. Results from experiments in which ordinary rubber-stoppered flasks were used agree so well with those for experiments with the special flasks that the ordinary ones have been used for most liquid chemicals having boiling points above about 35° C. By weighing 40- to 50-milliliter volumes of sulfur dioxide measured into a small partially evacuated flask from the gas burette in use for these experiments, it was found that the errors of three determinations were respectively 3.4, 2.6, and 1.0 per cent of the weight.

The specific gravity of each chemical was determined with few exceptions at a temperature within a degree or two of that at which the material was measured into the fumigation flasks. Slight errors have no significant effect upon toxicity calculations.

The various insect species used in these tests were cultured in a basement laboratory, the temperature of which varies within rather narrow limits from about 22° to 26° C. For each individual test a group of from 30 to 60 active insects was placed in a cylindrical cage of silk bolting cloth or fine wire screen which was hung by a thread in the fumigation flask. All tests were made in constant temperature chambers. The moisture of the air was not controlled, but was rather uniformly low, probably from 25 to 40 per cent relative humidity.

A serious source of variation in the results lies in the difficulty in distinguishing a sharp endpoint. By what signs shall the insects be known as dead? It is believed that the endpoint chosen should be such that the estimated mortality will represent the eventual result as nearly as possible. It appears necessary in the case of the average fumigant that the estimate be made at the end of about 40 hours, when many dying insects can still perform more or less conspicuous movements. Some chemicals are very slow acting or anesthetic. Others are so paralyzing that at the end of 40 hours the insects are separated easily into active walkers and darkened, desiccated remains. Peculiarities of each insect species and stage further complicate the choice of endpoint. In general it has been the practice in the work reported in this bulletin to choose an endpoint indicative of the eventual effect upon the population. Hamlin and Reed (1927) reported that several larvae of *Plodia interpunctella* (the Indian-meal moth) revived a week or more after fumigation with carbon disulfide, and developed later to the adult stage. Hence it is important to allow both for recovery by resistant species as well as for tardy mortality by slow-acting chemicals.

THE RELATIVE TOXICITY OF FUMIGANTS TO VARIOUS INSECTS

In Table 1 are given the median toxicities of most of the insect fumigants recommended by entomologists or to be found on the market. Three common and easily reared pests have been used as test insects in this comparison: the confused flour beetle *(Tribolium confusum* Duval*)*, the granary weevil *(Sitophilus granarius* L.*)*, and the rice weevil *(Sitophilus oryzae* L.*)*. The first is the most important pest of flour mills in Minnesota, whereas the granary weevil is the one most important in Minnesota grain elevators. The rice weevil is sometimes brought into the state in shipments of grain from the south, where it is the more abundant of these similar and closely related pests. The flour beetle is not a near relative of the weevils (or true snout beetles). Usually from 1,000 to 1,500 insects have been used in determining each mortality curve, altho some curves have involved more or less than these numbers. Altho tests were made with equal care, the estimation of dosages from curves involving small amounts of a chemical is more precise than from those involving relatively large amounts. Whereas the difference of 1.1 milligrams per liter in the median dosages of chloropicrin and sulfur dioxide against the flour beetle is significant, the same cannot be said for a difference of 2 milligrams in those dosages of the methyl and ethyl acetates against the granary weevil.

The most precise estimate of relative dosages from a sigmoid mortality curve is that made at the point of 50 per cent kill. Because of this fact, many median dosages have been published. Precision thus obtained is often of distinct advantage in theoretical studies of the various factors that influence toxicity. The median lethal dose is an unsatisfactory basis, however, for determining the relative practical values of fumigants. The respective mortality curves are seldom parallel; in fact they may even cross between the points of 50 and 100 per cent mortality. Even tho estimates at a point near 100 per cent mortality are less precise than those at 50 per cent, it seems best to utilize the former in discussing the practical application of fumigants.

Statistical considerations make it inadvisable to attempt comparisons of dosages that produce complete kill if each dosage is estimated from the upper end of a toxicity curve. By means of the following equation (Shepard, 1934), an estimate is calculated from two points on a more reliable part of the experimental curve, i.e., the points of 50 and 90 per cent mortality.

$$x = K + k \cdot \log \frac{y}{100\text{-}y},$$

when K is the dosage to produce 50 per cent mortality and k that to produce 90 per cent; x and y are the values for dosage and mortality, respectively.

Table 1. Median Toxicity to Certain Insects of the Various Chemicals in Use or Sometimes Suggested for Use as Insect Fumigants; Temperature, 25° C.; Exposure Period, Five Hours

Fumigant	Boiling point* (°C.)	Mg./liter to kill 50 per cent		
		Tribolium confusum	*Sitophilus granarius*	*Sitophilus oryzae*
Hydrocyanic acid	26	0.6	5.8	.....
Chloropicrin	112	4.6	5.0	2.0
Sulfur dioxide	—10	5.7	5.7	17
Ethylene oxide	11	18	5.6	5.7
Carbon disulfide	46	61	40	26
Methyl formate	32	23.5	20	.....
Ethyl formate	54	24.5	29	17.5
Methyl bromide	5	11.2	7.4	4.0
Methyl acetate	57	82	88	63
Ethyl acetate	77	83	86	49
Ethylene dichloride	84	37.5	138	31
Propylene dichloride	97	40	118	44
tert.-Butyl alcohol	83	43	73	32
Trichlorethylene	87	108	335	196
Carbon tetrachloride	76	185	360	160
Furoyl chloride	176	9	2.6	.....

* These boiling points are taken from the Handbook of Chemistry and Physics, 20th edition.

In Table 2 are given the dosages calculated to kill 99 per cent, or practically the entire population. The estimates in milligrams per liter may be divided by 16.4 to obtain the same values in terms of pounds per

1,000 cubic feet. The results given in Tables 1 and 2 indicate that the order of toxicity may be very different for species that are structurally so different as *T. confusum* and *S. granarius,* whereas it is the same with few exceptions in the case of closely related species *(S. granarius* and *S. oryzae).*

Mortality curves showing the interaction of insect and fumigant sometimes are reliably constructed from relatively few experiments, the insects being definitely alive or dead within a reasonable time after treatment. On the other hand, some fumigants give results not so easily evaluated with nearly all the species of insects tried. Furthermore, some species of insects are less easily separated into survivors and non-survivors than others. *Tribolium confusum* appears to be a more desirable test insect in this respect than many others. In the case of either carbon disulfide or chloropicrin, repetition of the mortality curve shows much less variation than for ethylene dichloride. It appears that variations in results do not depend alone upon variations within the population and its environment, but to a considerable extent upon the specific reaction of that population to a certain toxic agent.

Table 2. Dosages Calculated to Kill 99 Per Cent of the Insects; Temperature, 25° C.; Exposure Period, Five Hours

Fumigant	Mg./liter to kill 99 per cent		
	Tribolium confusum	*Sitophilus granarius*	*Sitophilus oryzae*
Hydrocyanic acid	1.1	11.4	.....
Chloropicrin	7.0	21.0	15.2
Sulfur dioxide	10.7	11.3	46.9
Ethylene oxide	31.2	11.2	7.5
Carbon disulfide	91	66	40.0
Methyl formate	37.5	36.0	.....
Ethyl formate	32.5	49.0	35.5
Methyl bromide	14.4	8.4	6.2
Methyl acetate	130	129	81
Ethyl acetate	123	178	71
Ethylene dichloride	73	246	137
Propylene dichloride	98	234	132
tert.-Butyl alcohol	67	109	60
Trichlorethylene	268	405	316
Carbon tetrachloride	405	859	559
Furoyl chloride	16.0	.....	.....

In Figure 2 are shown the percentages of mortality in groups of from 30 to 75 adults of *T. confusum* when exposed to different concentrations of either ethylene dichloride or carbon disulfide. The data were determined by two different workers over a period of several years. Further data, not plotted, are also in agreement, showing that a population may react rather uniformly to one toxic agent and not so uniformly to another. On the other hand, a considerable part of the apparent variation in the case of ethylene dichloride may be caused by the greater difficulty in distinguishing the endpoint than in the case of carbon disulfide. An indication of the agreement that may be obtained is given by Strand (1930).

It can be seen from Figure 3 that mortality curves for different fumigants are not necessarily parallel. In fact, they may cross each other as in the case of the curves for ethylene oxide and chloropicrin against the granary weevil. If the median toxicities were taken as the criterion of effectiveness, the two compounds would be rated as about equal in toxicity, whereas on the basis of higher percentages of mortality, ethylene oxide is definitely more effective under the given experimental conditions than chloropicrin. The relative positions of the several curves differ conspicuously for the two species concerned.

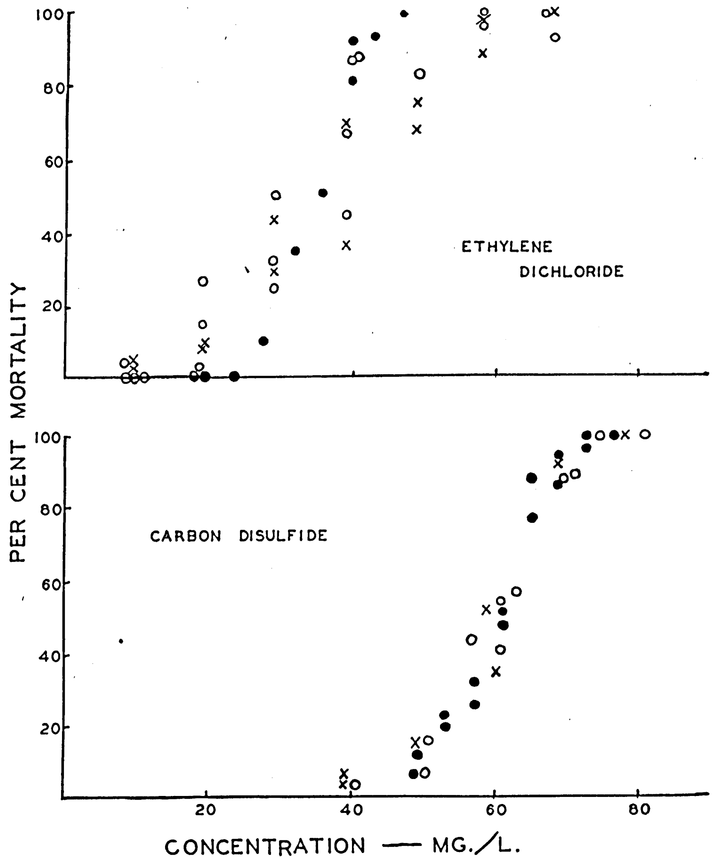

FIG. 2. RESULTS OF INDIVIDUAL EXPERIMENTS SHOWING THE DIFFERENCE IN VARIABILITY OF TWO FUMIGANTS AGAINST *T. confusum*

● .... Data from Strand (1930)
O .... Original data, 1931-32
X .... Original data, 1933

The dosage scale in Figure 3 is plotted in logarithms in order to avoid the distortion of the curves common when an arithmetic scale is used. The lower ranges are expanded while the higher ones are compressed, allowing more curves to be shown conveniently in a single figure. The curves are more symmetrical when drawn to a logarithmic scale.

The external factors that are most important in affecting toxicity results are temperature and moisture. Temperature effects will be discussed in subsequent paragraphs. Moisture has been little studied in this relation but appears (Lindgren and Shepard, 1932) to have no influence on the resistance of adults of *T. confusum,* whereas the resistance of eggs of that species is affected considerably.

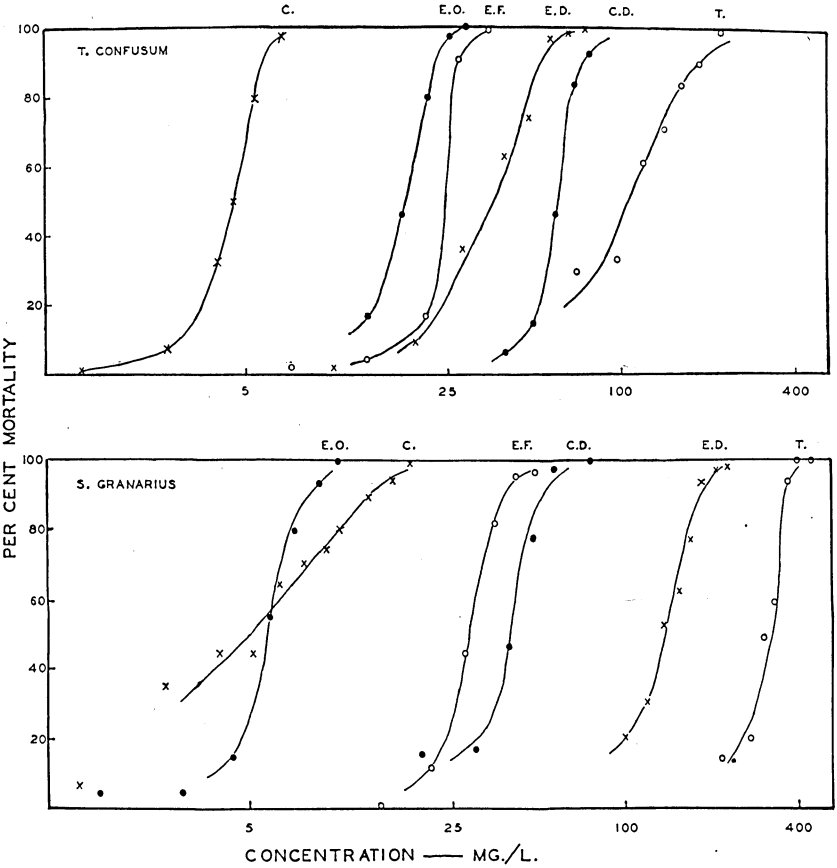

FIG. 3. MORTALITY CURVES FOR *T. confusum* AND *S. granarius* EXPOSED TO SIX FUMIGANTS FOR 5 HOURS AT 25° C.

C.	Chloropicrin	E.D.	Ethylene Dichloride
E.O.	Ethylene Oxide	C.D.	Carbon Disulfide
E.F.	Ethyl Formate	T.	Trichlorethylene

Such internal factors as the stage of development, even to the age of the pupa in days (Lindgren, 1935), are important in determining the susceptibility of an insect to a fumigant. The importance of the influence of different foods or of the degree of nourishment upon susceptibility is unknown.

Survivors of various exposures to both chloropicrin and ethylene dichloride were placed in flour and kept for eight months. In most cases numerous progeny were produced, altho no statement can be made as to whether reproductivity of the surviving individuals was normal.

Hydrocyanic acid.—Of the fumigants in use, hydrocyanic acid is the most important commercially as well as the most toxic to insects in general. It was used as early as 1877 to kill museum pests. There are various methods of producing the gas. The addition of either potassium or sodium cyanide to certain concentrations of sulfuric acid results in its rapid evolution. Atmospheric moisture reacts with calcium cyanide to produce the gas somewhat more gradually. The gas itself is manufactured and shipped as a liquid in metal containers. The boiling point is 25.7° C. (=78.3° F.), so the liquid is pumped into a sprayer system through which it is distributed into the space to be fumigated. Vaporization of such a low-boiling compound is very rapid. A variety of cyanide preparations are on the market in which liquid cyanide is absorbed in an inert carrier.

Few definite determinations of the toxicity of hydrocyanic acid have been made. Strand (1930) determined the median lethal dose for *T. confusum* as 0.607 milligrams per liter. The gas was generated from calcium cyanide, the exact concentration being determined at the conclusion of each experiment by washing out the fumigation flask with dilute sodium hydroxide and titrating with silver nitrate. One of the authors (Lindgren) has determined the median dose for the same insect, using liquid cyanide vaporized in a vacuum chamber with a capacity of a little over 100 cubic feet. In one series of tests 50 per cent of the insects were killed at 0.57 milligrams per liter and in a second series at 0.63 milligrams per liter, figures which agree very well with that given by Strand. Peters and Ganter (1935) determined rather carefully the concentration of hydrocyanic acid to kill 100 per cent of the granary weevil. Altho their data at 25° C. are not given, the value for five hours' exposure at this temperature is 1.2 volumes per cent, or about 13 milligrams per liter, as estimated from their curve. The corresponding value, determined in the 100-cubic-foot vacuum chamber, is 11.4 milligrams per liter. There is some evidence that somewhat higher dosages are required at low relative humidities.

Chloropicrin.—Chloropicrin is one of the "tear gases" used during the World War. Its insecticidal value was discovered by Moore (1917) in a study of the toxicity of various gases to the house fly. It was shown to be 168 times as toxic, molecule for molecule, as carbon disulfide (not 283 as has been frequently stated). Placed on a weight basis, the ratio is further reduced so that chloropicrin is 78 times as toxic to the house fly as carbon disulfide. Strand (1927) states that "it seems unwise to make any definite statement regarding the relative toxicities without limiting it by the factors of temperature and concentration." Not only these two factors must be taken into account but others such as the species of insect, its age or stage of development, its nourishment, and all the other variable conditions of each experiment that can be controlled. The ratio of toxicities to different species may vary widely. For instance, Pospelov *et al.* (1927) showed chloropicrin to be eight to ten times as toxic to *Sitophilus granarius* as carbon disulfide, a finding in good agreement with the median values recorded in Table 1. Our determinations indicate that for either *Tribolium confusum* or *T. castaneum* the ratio is about 13 times. Lehman (1933) determined the median lethal doses of various fumigants to kill wireworms at 25° C. His results indicate chloropicrin is 45.7 times as toxic as carbon disulfide under the conditions of his experiments. These citations show how unreliable are numerical ratios in statements of the relative toxicity of insect fumigants lacking in information relative to the important variable factors involved.

In general, chloropicrin is less toxic to insects than hydrocyanic acid, altho the difference is small enough so that some species may be found to be more easily killed by the former. In fact, Pospelov *et al.* state that chloropicrin is more toxic than hydrocyanic acid to *Bruchus chinensis,* a species of bean weevil.

Sulfur dioxide.—The fumes of burning sulfur, in other words, sulfur dioxide, have been employed as a fumigant for many centuries. Homer speaks of "pest-averting sulfur" and the "divine and purifying fumigation." Because fumigation with sulfur is an easy method commonly practiced, it seems of value to indicate the relative toxicity of sulfur dioxide.

This gas tarnishes various metals. It is highly soluble in water, producing a solution of sulfurous acid. It bleaches some dyes in wall paper and fabrics, altho it is likely that the damage does not occur extensively if the atmospheric moisture is low. It injures wheat or flour for bread. It affects seed germination. Because of some of the disadvantages of sulfur dioxide, it appears undesirable in mixtures with carbon disulfide, ethylene dichloride, or carbon tetrachloride, unless the content is so low that there is no appreciable effect other than an increase in insecticidal value.

It is highly interesting from the toxicological standpoint that the rice weevil is more resistant to sulfur dioxide than is the granary weevil. This is the only case thus far in which the rice weevil has been found to have greater resistance to a fumigant than the closely related granary weevil.

Ethylene oxide.—The fumigant value of ethylene oxide was discovered by Cotton and Roark (1928) during their study of many volatile organic compounds in this connection. Ethylene oxide is a product of the natural gas chemical industry. As its boiling point is low (10.5° C. = 50.9° F.), it is necessary to handle it in metal cylinders. To eliminate its inflammability in high concentrations, it is mixed with liquid carbon dioxide, the mixture being furnished in cylinders ready for use as an insect fumigant. Considerable experimental work has been done with the mixture under the name of "T-gas" by German workers.

Altho ethylene oxide is not nearly as effective against the flour beetle *(Tribolium confusum)* as chloropicrin, it is about equally toxic to the granary weevil. Lindgren and Shepard (1932) pointed out that whereas the eggs of *T. confusum* are much more resistant than the adult beetles to either chloropicrin or carbon disulfide, they are killed by only one-ninth the concentration of ethylene oxide necessary to kill the adults.

Ethylene oxide should not be used to fumigate seeds, for the available data indicate it affects seed germination.

Propylene oxide boils at about 35° C. (= 95° F.), considerably higher than ethylene oxide, and can be handled in the same type of container as ordinary ethyl ether. It is not as toxic as ethylene oxide but is still considerably better than carbon disulfide in this respect. It was included in the preliminary tests of Roark and Cotton (1929).

Carbon disulfide.—According to Simmons and Ellington (1926), the first use of carbon disulfide as an insect fumigant was by Garreau who published in 1854 the results of experiments with various compounds against the granary weevil, "sulfure de carbone" being reported best. Since about 1880 its use in this country has steadily increased altho the earlier reports refer chiefly to its value as a soil insecticide and in control for rats, gophers, and ants. Chittenden (1896) recommended the use of carbon disulfide in general fumigations of stored products in warehouses. Prior to this time heat treatment of stored products was relied upon largely in the control of insects. Hinds (1909, 1910) extended the use of carbon disulfide, especially in the southern United States, through his experiments with it in the control of insects in stored corn.

The use of carbon disulfide in buildings is very objectionable, because it is inflammable and small quantities mixed with air form a highly explosive mixture. The Underwriters' Laboratories rate carbon disulfide as considerably worse than gasoline or even ether as a fire hazard. The majority of entomologists are inclined, however, to disregard the hazards of carbon disulfide. Their attention is directed to the following information given by the National Board of Fire Underwriters.

Regarding carbon disulfide, they say, "It is highly volatile, giving off vapors in flammable proportions at temperatures as low as 22 degrees below zero Fahrenheit. Its vapors may ignite spontaneously when raised to a temperature of 212 degrees Fahrenheit, so that there is danger of ignition from steam pipes and other moderately hot surfaces. Its vapors are 2.6 times as heavy as air so that they diffuse slowly and will collect in low spots and there persist for a considerable time. The flammable or explosive range of the vapors is from 1 to 50 per cent, in air by volume, i.e., when mixed with air within these proportions an explosive mixture results which may be ignited by a hot surface as stated above."

Hinds (1911) reported a case of an explosion of carbon disulfide within a few minutes of the time it was applied to heating unhusked corn.

Methyl and ethyl formates.—Methyl and ethyl formates were tested by Neifert *et al.* (1925), Cotton and Roark (1928), and Roark and Cotton (1929). At the present time methyl formate is to be obtained in cylinders in combination with somewhat over 90 per cent liquid carbon dioxide. The latter is used in rather large quantities so insects are killed by the combined toxic properties of the two gases. R. M. Jones (1935) has discussed such mixtures and their toxicity. Methyl formate boils at 32.3° C. (=90.1° F.).

Ethyl formate, according to Simmons *et al.* (1935), is at present a standard fumigant for individual-pack fumigation. It has a boiling point of 54.3° C. (=129.7° F.), making it a fairly easy fumigant to handle as a liquid under ordinary temperature conditions.

These two chemicals are more toxic than carbon disulfide to *T. confusum* and *S. granarius,* according to Table 1. Lehman (1933) recorded the same to be true for wireworms.

Methyl bromide.—Methyl bromide is a recent addition to the commercial fumigant field in this country, being used principally in combination with carbon dioxide. Le Goupil (1932) found it to be an effective fumigant by itself. It had been used previously to eliminate the fire hazard of certain liquid fumigants altho it actually possessed a much higher toxicity than the fumigants with which it was mixed. It appears to be somewhat more toxic to the granary weevil than hydrocyanic acid.

Methyl and ethyl acetates.—Neifert *et al.* (1925) recommended a mixture of ethyl acetate and carbon tetrachloride as a substitute for carbon disulfide for fumigating grain in box cars. A non-inflammable mixture, however, has low toxicity. Furthermore, the fumigated grain is liable to have a sour odor, resulting from the acetic acid formed by hydrolysis of the ethyl acetate (Roark and Cotton, 1929).

Methyl acetate appears to have about the same toxicity as ethyl acetate. Neither is nearly as effective as carbon disulfide against the insects for which data are given in Tables 1 and 2. Both are noticeably more toxic to the *Sitophilus* species than ethylene dichloride, but the latter is more so to *T. confusum.*

Ethylene and propylene dichlorides.—These compounds were tested by Neifert *et al.* (1925), and Roark and Cotton (1929). In 1927 Cotton and Roark recommended the use of a mixture of ethylene dichloride and carbon tetrachloride as a substitute for carbon disulfide. At the present time the standard mixture contains 75 per cent ethylene dichloride. It is the most important of the liquid fumigants for small-scale fumigation by the inexperienced user, especially for the control of clothes moths (Herrick and Griswold, 1932). The addition of 25 per cent by volume of carbon tetrachloride reduces the toxicity of ethylene dichloride so the mixture is about equal to carbon disulfide against *T. confusum.* In the case of the granary weevil, however, about five times as much of the mixture is required as of carbon disulfide. Propylene dichloride has a lower vapor pressure than ethylene dichloride, so is less effective under practical conditions.

tert.-Butyl alcohol.—Roark and Cotton (1929) found tertiary butyl alcohol has considerable toxicity. Their results, as well as those reported in Table 1, indicate that this compound is generally intermediate between ethyl formate and ethylene dichloride in this respect. It has been on the market as a non-inflammable mixture with carbon tetrachloride.

Carbon tetrachloride.—Altho carbon tetrachloride had been used previously for the fumigation of nursery stock, its first use as a fumigant of stored products was by Morse (1910). It was recognized right away that carbon tetrachloride is not nearly as effective as carbon disulfide. The larger quantities required to produce good results make its use much more expensive. For some years, however, it was the only fumigant generally used for grain fumigation where carbon disulfide could not be used because of the fire hazard.

Trichlorethylene.—Trichlorethylene is not inflammable. It would seem then that, because it is a more effective fumigant than carbon tetrachloride, it would be a better diluent or solvent for inflammable compounds. It has a somewhat higher boiling point. Mixtures of three volumes of ethylene dichloride with one of trichlorethylene are mentioned by Back and Cotton (1935).

Furoyl chloride.—Furoyl chloride is produced from furfural, a product of oat hulls. It is a powerful lachrymator, or "tear gas", and has been proposed as a fumigant for grain insect control. It has about the same toxicity as chloropicrin. It was very difficult to produce toxic concentrations. In fact, concentrations to kill over 75 per cent of a group of granary weevils were not secured.

The figures given for the toxicity of furoyl chloride to the flour beetle are quoted from a manuscript report by A. L. Strand. A sample used by the authors appeared to be a little less toxic. It boiled between 175 and 184° C.

Formaldehyde.—Altho successful use of formaldehyde as an insect fumigant has been reported a few times, in general this material is ineffective. Many inquiries are directed to the official entomologist, however, regarding its use, chiefly because persons asking their druggist for a fumigant are sold formaldehyde, irrespective of the organism it is to be used against.

THE TOXICITY OF NEW COMPOUNDS AS INSECT FUMIGANTS

In Table 3 are listed certain new compounds, chiefly chlorinated chemicals, with their relative toxicity for *Tribolium confusum* and *Sitophilus granarius*. Some of them are very toxic to these insects, being even more toxic than chloropicrin in some cases. The acid chlorides, represented here by acetyl, propionyl, and thionyl chloride (usually called sulfurous oxychloride), are such toxic chemicals but they are probably too active chemically to be suitable for use as fumigants. Dichlorethyl ether has a high boiling point (178° C.) and is retained by products fumigated with it.

Certain interesting relationships of toxicity and chemical constitution are indicated. The ethylene series and the methane series are toxic to *T. confusum* in opposite orders. The median lethal points for dichlorethylene (symmetrical), trichlorethylene, and tetrachlorethylene are 154, 108, and 55 milligrams per liter, respectively, whereas for dichlormethane (commonly called methylene chloride), trichlormethane (chloroform), and tetrachlormethane (carbon tetrachloride) they are 82, 157, and 185 milligrams per liter. It is well to point out here that the so-called ethylene dichloride is dichlorethane formed by the addition, rather than the substitution, of chlorine in the ethylene molecule. It does not differ much from trichlorethane in its toxicity to *T. confusum*. The sym.-dichlorethylene used was the *cis* form, for the *trans* form has a distinctly lower boiling point (48° C.). The toxicities of three dichlorethylenes as well as triand per-chlorethylene have been determined for the granary weevil and their relationship to the boiling points examined by Ferguson (1936).

Various workers have demonstrated the toxicity of thiocyanates as contact insecticides. It was of interest to investigate a low-boiling thiocyanate as a fumigant. Since the figures for methyl thiocyanate were determined as shown in Table 3, a report has been published by Lathrop *et al.* (1936) showing that this compound is highly toxic to the California red scale. Its boiling point (133° C.) is probably higher than should be the case with a fumigant.

Some of the sulfur substituted organic compounds also are proving to have value as contact insecticides. Hence the fair toxicity of ethyl thioacetate is of interest, altho its boiling point is somewhat high (116° C.) and it has a very disagreeable odor.

Table 3. The Relative Toxicity of Compounds Related to Fumigants; Temperature, 25° C.; Exposure Period, Five Hours

Compound	Boiling point (°C.)	*T. confusum* Mg./liter to kill 50 per cent	*T. confusum* Mg./liter to kill 99 per cent	*S. granarius* Mg./liter to kill 50 per cent	*S. granarius* Mg./liter to kill 99 per cent
Propylene oxide	35	32	52	25	41
Acetyl chloride	52	3.6	5.6	......	......
Propionyl chloride	80	4.1	8.3	5.0	14.0
Thionyl chloride	79	2.0	3.8	3.0	9.0
a b-Dichlorethyl ether	140	2.1	3.1	1.7	4.7
b b-Dichlorethyl ether	178	1.8	3.5	1.7	3.7
Chlormethyl ether	58-60*	3.3	10.3	......	......
sym.-Dichlormethyl ether	100-108*	10.2	14.2	......	......
Methylene chloride	40.5-42*	82	182	......	......
sym.-Dichlorethylene	58-61*	154	303	......	......
Tetrachlorethylene	119-121*	55	99	......	......
1-1-2-Trichlorethane	110-117*	38.5	60.5	......	......
Chloroform	61	157	267	240	660
Methyl thiocyanate	130-131*	1.6	2.6	3.5	5.7
Ethyl thioacetate	115-116*	45	63	20	34

* Sample from the Eastman Kodak Company; boiling point quoted from their price list.

THE RELATIVE SUSCEPTIBILITY OF DIFFERENT SPECIES TO FUMIGANTS

The relative susceptibility of *Tribolium confusum, Sitophilus granarius,* and *S. oryzae* to a number of compounds has been discussed. A few other species have been compared with them with respect to their susceptibility to chloropicrin, carbon disulfide, and ethylene dichloride. The data are given in Table 4.

It has been noted by Hase (1932) that both the eggs and adults of the tropical bedbug, *Cimex rotundatus,* are killed more readily by ethylene oxide than are those stages of the common bedbug, *C. lectularius.* Of the insects listed in Table 4, *Tribolium castaneum* and *Sitophilus oryzae* require higher temperatures for their development and are found in warmer climates than *T. confusum* and *S. granarius.* For the few cases involved there is a fairly consistent correlation of increased susceptibility to fumigants with the requirement for a higher developmental temperature. Until many more data are available, it is unwise to speculate further along this line. One other case of a similar differential mortality was reported by Gortner (1913) who found *Tenebrio molitor* to be more resistant to high concentrations of carbon dioxide than *T. obscurus*.

Table 4. The Median Toxicity of Chloropicrin, Carbon Disulfide, and Ethylene Dichloride to Various Insects; Temperature, 25° C.; Exposure Period Five Hours

Insect	Chloro-picrin	Carbon disulfide	Ethylene dichloride
	mg./liter	mg./liter	mg./liter
Tribolium confusum	4.6	61	37.5
Tribolium castaneum	2.4	28	....
Sitophilus granarius	5.0	40	138
Sitophilus oryzae	2.0	26	31
Oryzaephilus surinamensis	1.4	34	....
Bruchus obtectus	<1.3	22	72

THE RELATION OF TOXICITY TO TEMPERATURE

Temperature affects the action of a fumigant in several ways. The volatility of the fumigant increases with rising temperature, whereas the surface adsorption decreases. There are changes in the physiological state of the insect, with corresponding changes in susceptibility to the fumigant, with varying temperature.

The last factor was noted by Bertrand *et al.* (1919) when they found the action of chloropicrin on grain weevils to be accelerated by a small rise in temperature. Strand (1927) showed the time to kill *Tribolium confusum* with carbon terachloride must be increased as much as five or six times if the temperature is lowered from 35° to 25° C. For carbon disulfide the necessary increase in the time of exposure was only two or three times, and for chloropicrin about two times.

Four fumigants were studied with respect to the effect of temperature changes upon their toxicity to *Tribolium confusum*. In Table 5 is given the number of insects used to determine each toxicity curve with the 50 per cent points from the curves. The 99 per cent mortality, calculated by the method previously mentioned, is also tabulated for each curve.

In those experiments at temperatures other than 20° and 25° C., the fumigation flasks containing the test insects were placed at the desired temperature for from 30 minutes to an hour. In this manner it was thought the insects would become sufficiently adjusted to the changed conditions before fumigation. After most of these tests were made, Cotton (1932) showed that, in experiments at 50° F., flour beetles that had been kept at that temperature for several days prior to the experiment required a dosage of 133 milligrams ethylene oxide per liter to kill 100 per cent, whereas for those that had been kept at room temperature (75° F.) only 53 milligrams per liter were required. It is desirable to investigate the rate at which this decrease in susceptibility takes place, but this has not yet been done. The effect upon the results shown in

Table 5 if the insects were kept longer at each temperature cannot be predicted.

Table 5. The Relation of Relative Toxicity of Insect Fumigants to Temperature; T. confusum Exposed for Five Hours

Fumigant	Temperature	Population	50 per cent kill	99 per cent kill
Chloropicrin:	35° C.	658	1.8 mg./l.	2.4 mg./l.
	30	879	2.8	5.0
	25	1406	4.6	7.0
	20	762	5.9	9.9
	15	952	7.1	12.3
	10	670	11.5	15.7
	5	1052	7.8	15.4
	0	634	4.6	8.6
Carbon disulfide:	35	531	32	40
	30	520	44	68
	25	1472	61	91
	20	728	76	108
	15	1445	86	140
	10	802	154	280
	5	796	140	270
Ethylene dichloride:	35	1320	40	60
	30	848	39	57
	25	1292	38	73
	20	784	37	87
	15	829	60	120
	10	854	80	140
	5	1224	62	138
	0	697	48	78
Carbon tetrachloride:	35	615	75	225
	30	1581	125	490
	25	741	185	405
	20	696	225	564
	15	924	230	589
	10	569	250	535
	5	(Incomplete evaporation below 50 per cent kill)		

It will be noted that ethylene dichloride is very little affected by the change in temperature from 20° to 35° C., particularly if median lethal concentrations are compared.

From the theoretical standpoint these data (Table 5) have considerable significance in that, at the lower temperatures, it may be the combined effects of two toxic agents that are observed. Altho a temperature of 0° C. by itself produces 50 per cent mortality only after some days, apparently it exerts lethal action in five hours sufficient that only as much chloropicrin need be used as is required to give 50 per cent kill by its own action at 25° C. Peters and Ganter (1935) pointed out that at 0° C. lower concentrations of hydrocyanic acid are necessary to kill the granary weevil than at 17°, giving as the reason the fact that the physiological condition of the insects is very different at the two temperatures.

It is this interaction of two toxic agents that is utilized in certain commercial fumigants, consisting chiefly of carbon dioxide combined with a relatively low percentage of a more toxic chemical. The carbon

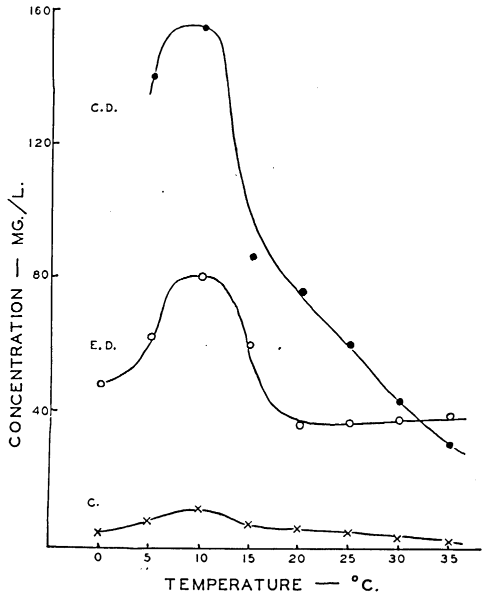

FIG. 4. EFFECT OF TEMPERATURE UPON MEDIAN LETHAL CONCENTRATIONS OF CHLOROPICRIN, ETHYLENE DICHLORIDE, AND CARBON DISULPHIDE FOR *T. confusum*

C. .... Chloropicrin
E.D. .... Ethylene Dichloride
C.D. .... Carbon Disulfide

dioxide concentration introduced in the fumigated space is not great enough to kill the insects, but the addition of the second ingredient, also at a sublethal concentration by itself, builds up the toxicity of the mixture enough to make it effective.

Recently Moore (1936) showed that the mortality of an insect may be greater at the lower temperatures which favor the adsorption of the gas rather than the higher ones which favor its chemical and physiological action.

Surface adsorption of fumigants on treated products is known to be greater at lower temperatures, altho no quantitative data are available. It is possible that the increase in adsorption may be enough to more than offset the increased efficiency of fumigants at temperatures below 10° C. Until more complete data are available regarding adsorption, the increased toxicity of some fumigants at low temperatures cannot take any certain place in recommended fumigation practice.

FUMIGANT PENETRATION

The efficiency with which a space may be fumigated with a liquid chemical depends, among other things, on the vapor pressure, or tendency to vaporize, inherent in the fumigant. At 25° C. (=77° F.) water and chloropicrin have about the same vapor pressure whereas ethylene dichloride has a pressure 3.4 times, carbon tetrachloride 4.9 times, and carbon disulfide 15.2 times as great. Those fumigants which normally exist as gases at the temperature of fumigation are not limited in this way. Their introduction into a given space depends upon the equipment used.

The concentrations of various fumigants which can exist in vapor form in a 1,000-cubic-foot fumigation chamber are given by Roark and Nelson (1929). The concentration of carbon tetrachloride (52.4 pounds per 1,000 cubic feet) to kill completely a population of granary weevils is near the limit given by them, i.e., 59.1 pounds at 25° C.

After the fumigant is vaporized, the problem becomes one of diffusion. Mass movement by air currents, as distinct from true molecular diffusion, is responsible to a large extent for equalizing the gas concentration in a room. This is probably especially true of the warm hydrocyanic acid gas rising from a generator jar containing acid and cyanide, or of the heavy vapor falling from a dish of carbon disulfide suspended in the upper part of a room. To distribute a liquid fumigant by sprinkling or spraying it around the room, or to circulate the fumigant with a fan, aids in its uniform mixture with the air.

At the same time that the fumigant is mixed with the air by current movement, molecular diffusion takes place, altho more slowly. "When two or more gases come in contact with one another, each will flow into the space, filled by the others, even when they are both under the same pressure. . . . The diffusion takes place most quickly with gases of small molecular weight, the particles of which have consequently greater velocities," Meyer (1892). Hence, those fumigants which diffuse most readily must be those of lowest molecular weight (see Table 6). Hydrocyanic acid, carbon dioxide, and ethylene oxide have much lighter molecules than chloropicrin, carbon tetrachloride, and ethylene dichloride, so other conditions being equal, they will diffuse more rapidly.

Table 6. Molecular Weights of Some Chemicals Discussed as Insect Fumigants

Fumigant	Molecular weight	Fumigant	Molecular weight
Ammonia	17	Carbon disulfide	76
Hydrocyanic acid	27	Methyl bromide	95
Formaldehyde	30	Ethylene dichloride	99
Carbon dioxide	44	Furoyl chloride	130
Ethylene oxide	44	Trichlorethylene	131
Methyl formate	60	Dichlorethyl ether	143
Sulfur dioxide	64	Carbon tetrachloride	154
tert.-Butyl alcohol	74	Chloropicrin	164

The extent to which molecular diffusion must be relied upon depends on the freedom with which mass movements of the atmosphere may take place. Diffusion is of great importance in the penetration of furniture and package goods by the gas, as well as being an important factor in the loss of the fumigant through the walls of buildings.

There are two opposing forces which determine the penetration of a fumigant into the goods to be treated. Diffusion tends to carry the gas into the interstitial spaces, the rate depending upon the molecular weight of the fumigant as just mentioned, and upon the size of the openings through which the fumigant passes. Opposing the diffusion of the gas is the adsorptive capacity of the product into which diffusion is in progress. Not only are the spaces between the particles of fumigated material filled with a mixture of gas and air, but each particle attracts a layer of gas molecules to its surface. The adsorptive capacity of a product, often very great, must be satisfied before a constant concentration can be maintained in the surrounding atmosphere. Hence we should not only know the relative toxicity of a fumigant for the insects but the adsorptive capacity of the product.

Cotton (1930) found that, in an empty vacuum tank, two ounces of chloropicrin per 100 cubic feet were required to give 100 per cent kill of *Tribolium confusum* adults in two hours at 72° F. When the tank was filled with raw peanuts, it was impossible to obtain 100 per cent kill even when the dose was raised to 48 ounces. Ethylene oxide did not appear to be adsorbed so much by the nut meats. In the empty tank 3.2 ounces per 100 cubic feet were required, and in the filled tank 11.2 ounces, to give 100 per cent kill in two hours.

A toxicity experiment was arranged so the relative adsorptive capacities of wheat and flour for ethylene dichloride were indicated. Three sets of six-liter fumigation flasks were used, one empty, the second containing a two-inch layer of wheat, and the third a similar layer of extra fine whole wheat flour. The material in each case had a volume of 128 cubic inches (the wheat weighing 1,600 grams, and the flour 1,020 grams) with an exposed surface of 375 square centimeters. The test insects contained in screen cages were hung about three inches above the surface of the flour or grain. In one set of experiments with flour in the flasks the fumigant was sprinkled directly on the flour, in a second set on filter paper laid on the flour. The mortality was a little lower in the second case, altho it is doubtful if the difference is significant. The results are shown in Table 7. The median lethal concentration of ethylene dichloride in the presence of wheat appears to be about twice, and in the presence of flour about eight times, that in the empty flasks.

Altho many previous workers had recognized the difficulty of securing good penetration with insect fumigants, Strand (1927) was the first

Table 7. The Toxicity of Ethylene Dichloride to Tribolium confusum in the Presence of Wheat and Flour; Temperature, 25° C.; Exposure, Five Hours

Adsorptive material	Concentration of fumigant	Population	Per cent mortality
None	19.5 mg./l.	40	12.5
	29.2	75	18.7
	30.1	35	37.1
	38.9	56	30.4
	40.2	42	61.9
	47.9	64	46.9
	50.2	59	79.7
	57.5	24	95.8
	68.1	54	98.1
Wheat	40.2	60	3.3
	50.2	50	10.0
	60.3	94	25.5
	80.4	36	72.2
	80.4	42	50.0
	100.5	53	88.7
	120.6	51	98.0
Flour	80.4	39	2.6
	80.4	53	0.0
	160.8	54	14.8
	160.8	43	7.0
	321.6	63	58.7
	321.6	50	46.0

one to measure penetration in any extensive series of controlled experiments. His principle contribution was to the effect that, contrary to the general belief, the heavier fumigants such as carbon disulfide and chloropicrin do not sink down very far in a mass of grain. Their concentration "varies inversely with the depth below the surface of the grain. Adsorption of the gases by the top layers of grain prevents their rapid downward movement."

When ventilation of a treated room is begun, the concentration of fumigant becomes less in the open spaces and diffusion into the fumigated products is reversed. The gas may be as slow in diffusing out as it was in going in. The outward rate depends upon the same factors as the inward. Since rather low concentrations of toxic gas may be lethal if the exposure is long enough, the fumigant may be retained sufficiently to be effective in killing insects within a treated product even if penetration was relatively slow. Safro (1927) pointed out the advantages of the retained fumigant in products that have been treated and not unpacked immediately.

SUMMARY

The relative toxicity of most of the insect fumigants in commercial use is reported for the confused flour beetle and two species of grain weevils. Various factors that affect the results are considered. Some of the advantages and disadvantages of each compound are mentioned.

Some new compounds of high toxicity were investigated, as well as a number of chlorinated compounds closely related to those in common use. The latter arrange themselves in an orderly manner with respect to their relative toxicity and their chemical constitution. Methyl thiocyanate has noteworthy toxicity greater than that for chloropicrin and approaching that for hydrocyanic acid.

An apparent correlation of developmental temperatures and susceptibility to fumigants is pointed out in the case of some closely related insect species.

The lower the temperature the less effective is a fumigant, to a certain point. Below about 10° C. (50° F.) the fumigant, however, becomes more effective the lower the temperature. This effect seems to be caused by the interaction of sublethal low temperature and low concentrations of the fumigant.

The rôle of adsorption in the fumigation of stored goods, as well as their penetration by the fumigant, has been discussed. The relative importance of adsorption in fumigant problems is indicated by the results of preliminary experiments.

LITERATURE CITED

BACK, E. A., and COTTON, R. T. (1935). Industrial fumigation against insects. U. S. Dept. Agri. Circ. 369. 52 pp.

BERTRAND, G., BROCQ-ROSSEU and DASSONVILLE. (1919). Influence de la temperature et d'autres agents physiques sur le pouvoir insecticide de la chloropicrine. Compt. rend. Acad. Sci., **169**:1059-1061.

CHITTENDEN, F. H. (1896). Some insects injurious to stored grain. U. S. Dept. Agriculture Farmer's Bulletin 45. Revised 1897.

COTTON, R. T. (1930). Carbon dioxide as an aid in the fumigation of certain highly adsorptive commodities. Jour. Econ. Ent. **23**:231-233.

———. (1932). The relation of respiratory metabolism of insects to their susceptibility to fumigants. Jour. Econ. Ent., **25**:1088-1103.

COTTON, R. T., and ROARK, R. C. (1927). Ethylene dichloride—carbon tetrachloride mixture; a new non-burnable non-explosive fumigant. Jour. Econ. Ent., **20**:636-639.

———. (1928). Fumigation of stored product insects with certain alkyl and alkylene formates. Ind. and Eng. Chem., **20**:380.

———. (1928). Ethylene oxide as a fumigant. Ind. and Eng. Chem., **20**: 805.

FERGUSON, J. (1936). Relation between the toxicities and the boiling points of related substances. Nature, **137**:361-362.

GORTNER, R. A. (1913). Notes on a differential mortality observed between *Tenebrio obscurus* and *T. molitor*. Amer. Nat., **47**:572-576.

HAMLIN, J. C., and REED, W. D. (1927). Insect revival after fumigation. Jour. Econ. Ent., **20**:400-428.

HASE, A. (1932). Über die unterschiedliche Widerstandsfähigkeit der parasitären Hauswanzen *Cimex lectularius* und *Cimex rotundatus* gegenüber der Einwirkung von Äthylenoxid; nebst Bemerkungen über die Wirkung von Äthylenoxyd auf Meerschweine. Zeits. f. wiss. Biol., Abt. F., Zeits. f. Parasitenk., **4**:369-386.

HERRICK, G. W., and GRISWOLD, G. H. (1932). Fumigation of the immature stages of clothes moths and carpet beetles with a mixture of ethylene dichloride and carbon tetrachloride. Jour. Econ. Ent., **25**:243-248.

HINDS, W. E. (1909). Carbon di-sulfide fumigation of grain infesting insects. Jour. Econ. Ent., **2**:161-165.

———. (1911). Carbon disulfide explosion from heated corn. Jour. Econ. Ent., **4**:532-535.

HINDS, W. E., and TURNER, W. F. (1910). Carbon disulfide fumigation for the rice weevil in corn. Jour. Econ. Ent., **3**:47-56.

JONES, R. M. (1933). A precise method for determining the toxicity of mixed gases to insects. Jour. Econ. Ent., **26**:895-902.

———. (1935). The toxicity of carbon dioxide–methyl formate mixtures to the confused flour beetle (*Tribolium confusum* Duv.) *Jour. Econ. Ent.* **28**: 475-485.

LATHROP, F. H., CUPPLES, H. L., HILEY, J., and YUST, H. R. (1936). Comparative toxicities of methyl thiocyanate and hydrocyanic acid to the California Red Scale. Jour. Econ. Ent., **29**:410-412.

LE GOUPIL. (1932). Les propriétés insecticides du bromure de méthyle. Rev. Path. Vég., **19**:169-172. (Rev. Appl. Entomol., **23A**:194.)

LEHMAN, R. S. (1933). Laboratory experiments with various fumigants against the wireworm *Limonius (Pheletes) californicus* Mann. Jour. Econ. Ent., **26**: 1042-1051.

LINDGREN, D. L. (1935). The respiration of insects in relation to the heating and the fumigation of grain. Minn. Agr. Expt. Sta. Tech. Bull. 109. 32 pp.

LINDGREN, D. L., and SHEPARD, H. H. (1932). The influence of humidity on the effectiveness of certain fumigants against the eggs and adults of *Tribolium confusum* Duv. Jour. Econ. Ent., **25**:248-253.

MEYER, V. (1892). Outlines of theoretical chemistry.

MOORE, WILLIAM. (1917). Volatility of organic compounds as an index of the toxicity of their vapors to insects. Jour. Agri. Research, **10**:365-371.

__________. (1936). Differences between resistant and non-resistant red scale in California. Jour. Econ. Ent., **29**:65-78.

MORSE, A. P. (1910). Carbon tetrachloride vs. carbon disulfide. Jour. Econ. Ent., **3**:104.

NEIFERT, I. E., COOK, F. C., ROARK, R. C., TONKIN, W. H., BACK, E. A., and COTTON, R. T. (1925). Fumigation against grain weevils with various volatile organic compounds. U. S. Dept. of Agriculture Dept. Bulletin 1313, 40 pp.

PETERS, G., and GANTER, W. (1935). Zur Frage der Abtotung des Kornkäfers mit Blausäure. Zeit. f. angew. Ent., **21**:547-559.

POSPELOV, V. P., SOLDAU, P., PETROV, A. D., and ISACHENKO, V. B. (1927). (The fumigation of grain and of meal with chloropicrin and other volatile materials.) (In Russian with German summary.) (Reports Bureau Appl. Ent. Leningrad, 3.) (1:36-54.) (See abstracts in Biol. Abstracts, 4, no. 12519, and in Rev. Appl. Ent., **16A**:172.)

ROARK, R. C., and COTTON, R. T. (1929). Tests of various aliphatic compounds as fumigants. U. S. Dept. of Agriculture Tech. Bulletin 162, 52 pp.

ROARK, R. C., and NELSON, O. A. (1929). Maximum weights of various fumigants which can exist in vapor form in a 1,000 cubic foot fumigating chamber. Jour. Econ. Ent., **22**:381-387.

SAFRO, V. I. (1927). Adapting fumigation procedures to industrial needs. Jour. Econ. Ent., **20**:261-267.

SHEPARD, H. H. (1934). Relative toxicity at high percentages of insect mortality. Nature, **134**:323-324.

SHEPARD, H. H., and LINDGREN, D. L. (1934). The relative efficiency of some fumigants against the rice weevil and the confused flour beetle. Jour. Econ. Ent., **27**:842-845.

SIMMONS, P., BARNES, D. F., FISHER, C. K., DONOHOE, H. C., and FISHER, C. D. (1935). Dried fruit fumigation. U. S. Dept. of Agriculture, Mimeo. Circ. E353. 15 pp.

SIMMONS, P., and ELLINGTON, G. W. (1926). The discovery of the insecticidal property of carbon disulfide. Science, **64**:326-327.

STRAND, A. L. (1927). A comparison of the toxicity and the diffusion in a column of grain, of chloropicrin, carbon disulfide, and carbon tetrachloride. Minn. Agr. Expt. Sta. Tech. Bull. 49, 59 pp.

__________. (1930). Measuring the toxicity of insect fumigants. Ind. and Eng. Chem., Analyt. Edit., **2**:4-8.